

Long-Lived Excited States at Surfaces: Cs/Cu(111) and Cs/Cu(100) Systems

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One-electron and multielectron contributions to the decay of transient states in the Cs/Cu(111) and (100) systems are studied by a joined wave-packet propagation and many-body metal response approach. The long lifetime of these states is due to the Cu *L* and *X* band gaps which reduce the electron tunneling between Cs and Cu. In the (111) case, the decay is mainly by inelastic *e-e* interaction, whereas in the (100) case, electron tunneling is dominating. This accounts very well for the experimental findings [Bauer *et al.*, Phys. Rev. B **55**, 10 040 (1997) and Ogawa *et al.*, Phys. Rev. Lett. **82**, 1931 (1999)].

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The understanding of the dynamics of excited electrons at clean and adsorbate covered surfaces is a key point for a variety of surface processes. Excited transient states, localized on an adsorbate or on a projectile hitting the surface, are very often invoked as intermediate states in ion and neutral desorption, fragmentation, vibrational excitation of adsorbates or projectiles, scanning tunneling microscope manipulation of individual adsorbates, and chemical reactions [1–3]. The efficiency of these reaction mechanisms depends in a crucial way on the intermediate state lifetime. Very often, a short lifetime introduces a bottleneck in the reaction (see, e.g., Ref. [4]). The development of time-resolved-2-photon-photo-emission (TR-2PPE) experiments in the fs regime [5] allowed the direct study of the time evolution of transient states at surfaces. In particular, image states received much attention prompting detailed theoretical studies of their relaxation [6]. In the case of low coverage alkali adsorbates on Cu(111) and (100) [7–10], TR-2PPE studies revealed the presence of an excited state with a long lifetime. These excited states are interpreted as associated with an electron localized around the positive alkali ion core, i.e., as a transient neutral state of the adsorbate, strongly perturbed by the surface. The presence of an adsorbate induced long-lived state is a potentially very important result in that it opens the way to very efficient surface mechanisms involving these long-lived transient states. As a first example, photon induced Cs desorption from Cu(111), mediated by the long-lived excited state, has been invoked [10].

Lifetimes of alkali induced states on a free electron metal have been calculated by a few methods [11–13], yielding lifetimes below 1 fs for alkali-surface distances typical of chemisorption. This is much shorter than the

lifetime found on the Cu(111) and (100) surfaces, which reaches a few tens of fs [7–10]. It is thus of paramount importance to understand the origin and the characteristics of these long-lived states: Why are they much longer lived on certain Cu surfaces than on a jellium metal and how do they decay? The present theoretical study is devoted to the Cs/Cu(111) and Cs/Cu(100) systems, with the aim of determining the lifetime of the excited states in these two systems in a parameter-free approach, thus yielding answers to the above two questions.

When an alkali atom is brought in front of a free-electron metal surface, the one-electron tunneling between the atom and the metal is very efficient. For atom-surface distances typical of chemisorption, it results in a very fast decay of the alkali state by electron transfer to the metal [11–13], the so-called resonant charge transfer (RCT). Recently, a wave-packet propagation (WPP) study of various ions and atoms interacting with a Cu(111) surface [14] has shown how the peculiarities of the Cu electronic structure can influence the RCT; this has recently been confirmed experimentally in the context of collisional charge transfer [15,16]. The Cu(111) surface exhibits a projected band gap between -5.83 and -0.69 eV with respect to vacuum in the direction normal to the surface [-3.02 and $+3.08$ eV for Cu(100)] [17]. This is the preferential direction for the RCT process, and the projected band gap results in a very efficient blocking of the RCT for alkali adsorbate levels lying in its energy range. For the Cs/Cu(111) system, this leads to a very long lifetime of the adsorbate state, longer than experimental data. Usually, the one-electron transition terms are dominating over the other ones. In the present case, they are strongly reduced, and we show below that the multielectron terms (inelastic electron-electron

interaction inside bulk Cu) lead to significant decay rates; therefore, the decay of the excited state in Cs/Cu systems is due to the superposition of the one-electron and multielectron interactions. The difference between the Cs/Cu(111) and Cs/Cu(100) systems is also explained.

The present work is performed in two steps: (i) a WPP study of the Cs/Cu system which yields the one-electron decay rate and the wave function for the resonant state and (ii) the parameter-free calculation of the inelastic electron-electron decay rate using the wave function determined in step (i).

Details on the WPP approach can be found in Ref. [14]. It considers a single adsorbate on the surface and consists of directly studying the time evolution of an electron wave function in the compound potential formed by the superposition of an e^- surface, e^- -Cs $^+$ core, and e^- -Cs $^+$ core image interaction potentials. The model e^- -surface interaction potential is adjusted from an *ab initio* density functional theory study [17]; it considers only the modulation of the potential along the surface normal and assumes a free electron motion parallel to the surface. The e^- -Cs $^+$ core interaction is described by a pseudopotential of the Kleinman-Bylander form [18]. The Cs $^+$ core is located at $3.5a_0$ from the Cu(111) image plane [respectively, $3.0a_0$ for (100)], i.e., at a distance of $5.6a_0$ ($5.3a_0$) from the last Cu plane. This adsorption distance was deduced from the coverage dependence of the surface work function [19] or determined by experiment [20]. At these distances, we find that the Cs resonance is 1.98 eV (1.46 eV) below vacuum for Cu(111) [respectively, Cu(100)], which corresponds well to the experimental data of Refs. [7–10], extrapolated to a vanishing coverage. The electronic structure of the Cs/Cu systems in our study are schematically presented in Figs. 1(a) and 1(b). The one-electron decay is energy conserving and the Cs state can decay only to Cu states with the same energy, thus involving transitions to states with a large k_{\parallel} (momentum parallel to the surface). These are the surface or bulk states for the (111) surface and surface resonance and bulk states for the (100). This is in contrast with the case of a free electron metal surface, where transitions to $k_{\parallel} = 0$ states are possible.

The WPP procedure yields the energy and the one-electron decay rate of the transient state as well as its wave function Ψ . The latter is presented in Fig. 2 for Cs/Cu(111) and Cs/Cu(100). The Cs localized transient state is strongly polarized by its interaction with the surface, resulting in the repulsion of the electronic cloud away from the surface. The large stabilization at chemisorption distances is therefore an intricate combined effect of the band gap and of the polarization of the atom: (i) the band gap prohibits transitions to $k_{\parallel} = 0$ states which otherwise are dominating RCT, (ii) the shift of the electronic cloud decreases the overlap between the adsorbate and metallic wave functions, and (iii) most important, the hybridization of the adsorbate states strongly affects the transition probability as a function of k_{\parallel} which becomes narrower around

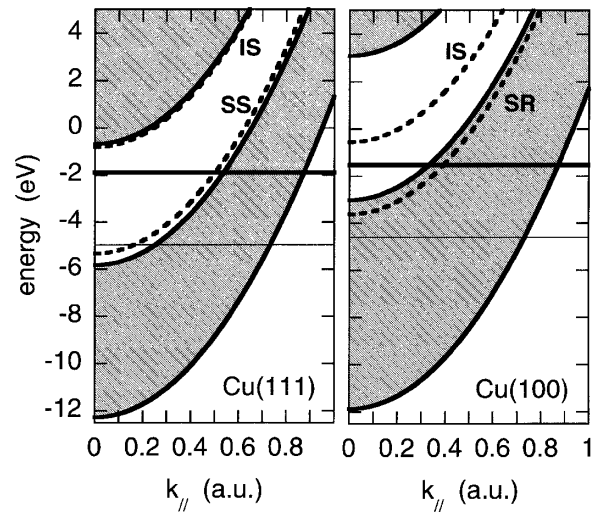


FIG. 1. Energy of the electronic states in the model Cu(111) and Cu(100) surfaces, as a function of the electron momentum parallel to the surface (k_{\parallel}). Vacuum is at zero energy. The 3D propagating states are represented by the hatched area. The surface and image states (dashed lines) are labeled SS and IS and the surface resonance on Cu(100) is labeled SR [$E = -5.33$ and -0.82 eV for (111) and $E = -3.62$ and -0.57 eV for (100)]. The thick horizontal line indicates the Cu states degenerate with the Cs transient state. The thin horizontal line gives the Fermi energy.

zero. This last point very efficiently reduces the decay to the surface state which otherwise is dominating the RCT decay on Cu(111) surfaces [14,16]. It is worth mentioning that without this strong polarization effect, a band gap does

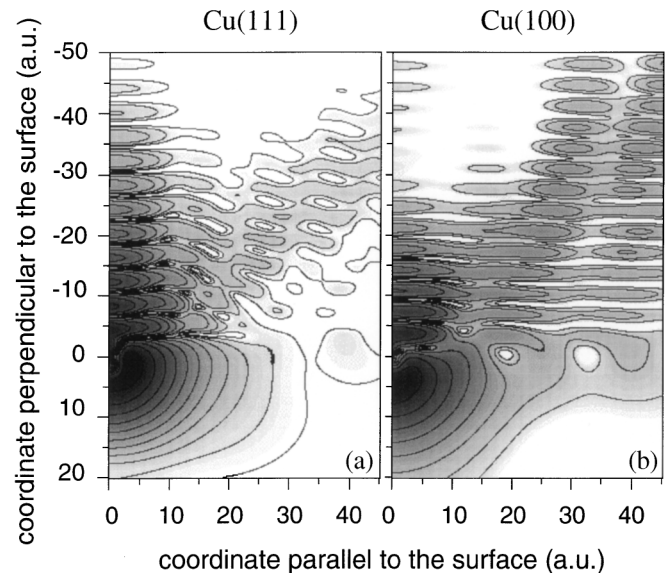


FIG. 2. Wave packet for the transient state in the Cs/Cu systems. It presents $\log(|\Psi|^2)$ in cylindrical coordinates: z , normal to the surface (positive in vacuum), and ρ , parallel to the surface. The dark areas correspond to large probabilities for the electron and the thin full lines to contour lines. (a) Cu(111), (b) Cu(100).

not always lead to a drastic reduction of the RCT rate at chemisorption distances [21]. As an illustration, preliminary results on the CO ($2\pi^*$) resonance on Cu(111) [21] do not show any stabilization in agreement with TR-2PPE data [1].

The resonance being long lived, the continuum part in Ψ is weak. The decay of the Cs resonance mainly populates the 3D propagating bulk states in the (111) case. Since a minimum k_{\parallel} is necessary for the transition (Fig. 1) and since the transition efficiency quickly decreases when k_{\parallel} increases, the decay to the 3D bulk states appears as a flux of electrons moving away around a well-defined angle from the surface normal. For Cu(100), besides the decay into the 3D bulk states, part of the outgoing electron flux occurs parallel to the surface and corresponds to the surface resonance state.

In the second step (ii), the wave packet Ψ is used to compute the inelastic electron-electron scattering contribution Γ_{ee} . This contribution is evaluated within the self-energy formalism of many-body theory [22,23]. Retaining the first term in the series expansion of Σ in terms of the screened Coulomb interaction W and replacing the full Green function G by the noninteracting Green function (GW approximation [22]), we obtain the following contribution to the linewidth of the excited state of energy E_0

$$\Gamma_{ee} = -2 \int \Psi^* \text{Im} \Sigma(\vec{r}, \vec{r}'; E_0) \Psi(\vec{r}') d^3 \vec{r} d^3 \vec{r}'. \quad (1)$$

The computation of the above integral is made very difficult by the loss of translational invariance parallel to the surface due to the adsorbate. To solve this problem, the self-energy of the Cs/Cu system is replaced by the self-energy of the clean Cu surface. This approximation is supported by the fact that both ingredients of the self-energy, namely, the final electron states and the screened interaction are mainly determined by bulk states which are not significantly affected by a single adsorbed Cs atom (only low Cs coverages are studied here).

The imaginary part of Σ has been evaluated for both Cu(111) and Cu(100) surfaces with the density response function computed within the random phase approximation [6]; both one-electron wave functions and energies

of final states are obtained with the model potential from Ref. [17]. All calculations are performed directly in real space. The self-energy is obtained by integrating the self-energy Fourier transform over the two-dimensional momentum space. Then, we integrate Eq. (1), using the axial symmetry of the problem.

Finally, Γ_{RCT} and Γ_{ee} are added to get the total decay rate Γ_T of the transient Cs/Cu state. This makes the implicit assumption that the one-electron decay is not influenced by the multielectron decay. This has been checked by performing WPP calculations in which the inelastic e^-e^- scattering is represented by an absorbing complex potential inside the bulk, by analogy with LEED studies [24]. The decay rate obtained in this way is the total decay rate Γ_T . Using an absorbing potential equal to the hot electron decay rate in bulk Cu [25] leads to results similar to those of the present two step calculation. In addition, it is found that the total decay rate varies linearly with the optical potential, showing that the two decays can be evaluated independently.

The two decay modes of the system are quite different. The RCT process populates substrate states with the same energy as the Cs resonance and with a large k_{\parallel} . The inelastic e^-e^- scattering leads to the population of substrate states with an energy lower than that of the Cs resonance. So, Γ_T is the *Cs resonance population decay rate* and not the energy decay rate of the system. Since the TR-2PPE experiments [7–10] are looking at electrons emitted close to the surface normal, large k_{\parallel} surface states and/or 3D bulk states populated by the RCT cannot be observed experimentally after absorption of the second photon and the measured decay rate is given by Γ_T .

The present decay rates, compared in Table I with experimental results [7–10], are seen to be quite consistent with the experimental data. One can stress that the difference between the two experimental results has been attributed to the difference in system temperature [9] (the theoretical results should correspond to a vanishing temperature). It is also worth noting that the present study is performed with a single adsorbate, whereas experiments concerned small finite coverages. Coverage changes have been shown not to dramatically change the RCT blocking effect [14] for low coverages; no similar study has been

TABLE I. Decay rates for the Cs/Cu(111) and Cs/Cu(100) systems.

Experiments	Cs/Cu(111)	Cs/Cu(100)
Transient state lifetime, Bauer <i>et al.</i> [7,8], 300 K	15 ± 6 fs	6 ± 4 fs
Transient state lifetime, Ogawa <i>et al.</i> [9,10], 50 K	50 fs	very short
Present results		
Free electron metal, Γ_{RCT}	900 meV	900 meV
Cu, Γ_{RCT} , one electron decay	7 meV	112 meV
Cu, Γ_{ee} , inelastic electron-electron decay	16.5 meV	20 meV
Cu, $\Gamma_T = \Gamma_{\text{RCT}} + \Gamma_{ee}$, total decay rate	23.5 meV	132 meV
Cu, transient state lifetime ($1/\Gamma_T$)	28 fs	5 fs

performed for the e - e interaction. The large difference between the two surfaces is well accounted for by our results, the (111) surface leading to the most stable state. Within the spirit of our 1D pseudopotential approach, the (110) surface should correspond to the free electron result, since there is no projected band gap along the normal. In this case, since the excited state can decay to bulk states around $k_{\parallel} = 0$, the measured lifetime should be dominated by the Cu bulk hot electron decay and transport effects. The large difference between the (100) and (111) surfaces can be understood by going back to the electronic structure shown in Fig. 1. The Cs state is lower by approximately 2 eV in the Cu(100) gap than in the (111) gap; this implies smaller k_{\parallel} values for the one-electron decay in the (100) case and thus a less efficient RCT blocking in this case (see discussions in Refs. [8] and [14]). This appears very clearly in Table I where Γ_{RCT} is much larger for the Cu(100) surface; it accounts for most of the difference between the two surfaces. We have checked that this difference is not a consequence of the change in adsorption height. On Cu(100), Γ_{RCT} varies only from 0.11 to 0.08 eV when the adsorption height is varied from $3.0a_0$ to $3.5a_0$.

We have reported on a parameter-free study of the decay of electronically excited states in the Cs/Cu(111) and Cs/Cu(100) systems. Using a joint wave-packet propagation and metal response approach, the very long lifetimes observed in these systems are well accounted for. The very long lifetimes are a direct consequence of the peculiarities of Cu electronic structure. The projected band gap of Cu(111) and (100) forbids the penetration of electrons along the surface normal and thus strongly decreases the efficiency of the one-electron decay of the transient states. This effect is further enhanced by the polarization of the transient Cs state. In Cs/Cu(111), one has a one-electron state localized on the Cs ionic core that is quasistable with respect to one electron transfer into the metal and that mainly decays by electron-electron interaction inside the bulk. This makes these Cs induced states the localized equivalent of the image states on the same surface. The situation is different in the (100) case, where the one-electron transfer to the metal is much more important and dominates the decay of the Cs induced state. The localized character of the Cs-induced states, together with their long lifetimes should make them very efficient intermediates promoting reaction mechanisms in adsorbate overlayers or in reactant collision with surfaces.

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